SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT	PAGE 1 of 16	
ENGINEERING AND COMPLIANCE	APPL. NO. 515638 & 515640	DATE: May 20, 2011
APPLICATION PROCESSING AND CALCULATIONS	PROCESSED BY S. JIANG	CHECKED BY D. GORDON

EVALUATION REPORT FOR PERMIT TO CONSTRUCT

Applicant's Name: RHODIA INC. Facility ID: 114801

Mailing Address: 20720 SOUTH WILMINTON AVENUE
LONG BEACH, CALIFORNIA 90810-1034

Equipment Location: 20720 SOUTH WILMINTON AVENUE
CARSON, CALIFORNIA 90810

EQUIPMENT DESCRIPTION

Appl. No. 515638 – New APC System - Caustic Scrubbers (Process 1, System 9) **Lead Application!**

Equipment	ID No.	Connected to	RECLAIM Source Type/ Monitoring Unit	Emission and Requirements	Conditions
Process 1: CHEMICAL MANUFACTURING, INORGANIC CHEMICAL					
System 1: SULFURIC ACID PLANT NO. 4					S13.1, S42.1, S42.2
FURNACE, WITH TWO LOW NOX BURNERS, FUEL OIL, NATURAL GAS, 2 SULFUR, 13 ACID BURNERS, 1 NOZZLE FOR VENT GAS FROM THE SPENT H2SO4 TANKS, WITH A/N: 474589 BURNER, FUEL OIL, NATURAL GAS, JOHN ZINK, TWO LOW NOX BURNERS, 75 MMBTU/HR EACH	D1	D18 D19 D20 D21 D86 D87 D88 D89 D90 D91 D115 D116 C124	NOX: MAJOR SOURCE**; SOX: MAJOR SOURCE **	**CO**: 2000 PPMV (5) [**RULE 407, 4-2-1982**] **H2SO4 MIST**: 0.15 LBS/TON PRODUCED (8A) [**40CFR 60 Subpart H, 10-17-2000; CONSENT DECREE CIVIL NO. 2:07CV134WL,7-23-2007**]; **H2SO4 MIST**: 0.3 LBS/TON PRODUCED (5) [**RULE 469, 5-7-1976**; RULE 469, 2-13-1981]; **H2SO4 MIST**: 10 PERCENT OPACITY (8B) [**40CFR 60 Subpart H, 10-17-2000**]: **PM**: (9) [**RULE 404, 2-7-1986**];**PM**:0.1 GRAINS/SCF (5) [**RULE 2011, 5-6-2005; RULE 409, 8-7-1981**]; **SO2**: 3.5 LBS/TON PRODUCED (5) [**CONSENT DECREE CIVIL NO. 2:07CV134WL,7-23-2007**] **SO2**: 4 LBS/TON PRODUCED (8A) [**40CFR 60 Subpart H, 10-17-2000**]	D82.1, D323.1
BOILER, WASTE HEAT AND 12 SOOT BLOWERS A/N: 474589	D2				
TOWER, GAS QUENCH A/N: 474589	D3				

COLUMN, STRIPPER, QUENCH ACID A/N: 474589	D6				
TOWER, GAS COOLING, PACKED TYPE A/N: 474589	D4				
COLUMN, STRIPPER, EFFLUENT WATER A/N: 474589	D5				
ELECTROSTATIC PRECIPITATOR, IN SERIES WITH DEVICE NO 8 A/N: 474589	D7	D8			
ELECTROSTATIC PRECIPITATOR, IN SERIES WITH DEVICE NO 7, COMBINED LOAD 160 KW A/N: 474589	D8	D7			
ABSORBER, DRYING, PACKED TYPE, WITH INTERNAL MIST ELIMINATOR A/N: 474589	D10	***C149***			
COMPRESSOR, MAIN PROCESS, CENTRIFUGAL A/N: 474589	D9				D82.2
REACTOR, CATALYTIC CONVERTER, HEIGHT: 66 FT; DIAMETER: 32 FT 6 IN A/N: 474589	D15				
ABSORBER, INTERMEDIATE, PACKED TYPE WITH INTERNAL MIST ELIMINATOR A/N: 474589	D11				
COLUMN, STRIPPER, PACKED TYPE, PRODUCT ACID A/N: 474589	D14				
ABSORBER, FINAL, PACKED TYPE, WITH INTERNAL MIST ELIMINATOR A/N: 474589	D13	***C148***			
~~**STACK, HEIGHT: 215 FT; DIAMETER: 6 FT**~~ ~~**A/N: 474589**~~	~~**S17**~~				~~**D82.3**~~
COOLING TOWER, WATER A/N: 474589	D16				
PIT, SULFUR, WIDTH: 24 FT; DEPTH: 6 FT 6 IN; LENGTH: 26 FT A/N: 474589	D130				
System 9: AIR POLLUTION CONTROL SYSTEM (NEW)					
SCRUBBER, SO2 SCRUBBER, 2 PACKED BEDS TOTAL, FIBER REINFORCED PLASTIC VESSEL, WITH MIST ELIMINATOR, HEIGHT: 61 FT; DIAMETER: 15 FT ***A/N: 515638***	***C148 (NEW)***	***D13***			***H23.2***

STACK, 130 FT ABOVE GRADE, 6 FT DIAMETER, A/N: 515638	*S151 (NEW)*				*D82.3*
SCRUBBER, PACKED BED, ACIDULATION STRIPPER, FIBER REINFORCED PLASTIC VESSEL, HEIGHT: 43 FT; DIAMETER: 3 FT 8 IN A/N: 515638	*C149 (NEW)*	*D10*			*C8.7, C12.1, D12.3, E57.3*
TANK, CAUSTIC SOLUTION, ELECTRICALLY HEATED, 7000 GALS; DIAMETER: 10FT; HEIGHT: 12 FT A/N: 515638	*C150 (NEW)*				

Appl. No. 515640 – Minor Title V Facility Permit Revision

"Revision of Title V Facility Permit per Rule 301(l)(7).

PERMIT CONDITIONS

C8.7 The operator shall use this equipment in such a manner that the flow rate being monitored, as indicated below, is not less than 40 gpm.

To comply with this condition, the operator shall monitor the flow rate as specified in condition number 12-3.

*[**RULE 2005, 5-6-2005; RULE 2011, 5-6-2005**]*

[Devices subject to this condition: C149]

C12.1 The operator shall use this equipment in such a manner that the liquid to gas ratio being monitored, as indicated below, is less than or equal to 0.07 gpm/cfm.

The operator shall install and maintain a liquid flow meter and a gas meter to accurately measure and record the:
1) total liquid flow in the stripper, in gallons per minute
2) gas flow rate at stripper gas inlet, in cubic feet per minute
(each recorded as 3-hour arithmetic average). In addition, the operator shall keep records, in manner approved by the District, for each of these parameters.

This maximum liquid to gas ratio shall not apply to periods of start-up or shutdown of the sulfuric acid plant for the first 1-year operation of this equipment provided all liquid and gas flow data during the start-up and shutdown periods are collected and submitted to the District within 30 days.

Start-up shall be defined as the first 12-hour period of operation of this equipment after sulfur bearing feeds have been introduced to the furnace, D1.

The shutdown shall be defined as the last 12-hour period of operation of this equipment before the compressor, D9, stops operation.

The operator shall notify the District whenever a start-up or shutdown occurs.

*[**RULE 2005, 5-6-2005; RULE 2011, 5-6-2005**]*

[Devices subject to this condition: C149]

D12.3 The operator shall install and maintain a(n) flow meter to accurately indicate the liquid flow rate in the stripper.

*[**RULE 2005, 5-6-2005; RULE 2011, 5-6-2005**]*

[Devices subject to this condition: C149]

D82.2 The operator shall install and maintain a CEMS to measure the following parameters:

SO_2 concentration (***by volume on a dry basis,*** 3-hour arithmetic average)

The CEMS shall be installed at the vertical straight duct on the suction side of the main gas blower, and shall sample in accordance with the requirements of the facility's EPA-approved Alternative Monitoring Plan.

The SO_2 concentration shall be used to demonstrate compliance with Condition S42.1.

The operator shall take all steps necessary to avoid CEMS breakdowns and minimize CEMS downtime. This shall include, but is not limited to, operating and maintaining the CEMS in accordance with best practices and maintaining an on-site inventory of spare parts or other supplies necessary to make rapid repairs of the equipment.

The CEMS shall be in operation during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the device D1, except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments).

The CEMS shall be operated and maintained in accordance with the applicable quality assurance procedures required by 40 CFR Part 60 Appendix F and SCAQMD Rule 2011 Appendix A.

For every hour of invalid data, missing data must be substituted following the procedures in District Rule 2011, Appendix A, Chapter 2, Section E – Missing Data Procedures.

[**RULE 1303(b)(2)-Offset, 5-10-1996;** RULE 1303(b)(2)-Offset, 12-6-2002; **CONSENT DECREE CIVIL NO. 2:07CV134WL, 7-23-2007**]

[Devices subject to this condition: D9]

D82.3 The operator shall install and maintain a CEMS to measure the following parameters:

SO_2 concentration (***by volume on a dry basis,*** 3-hour arithmetic average)

The SO2 concentration shall be used to demonstrate compliance with Condition S42.1.

The Operator shall sample stack emissions in accordance with the requirements of the facility's EPA-approved Alternative Monitoring Plan.

The operator shall take all steps necessary to avoid CEMS breakdowns and minimize CEMS downtime. This shall include, but is not limited to, operating and maintaining the CEMS in accordance with best practices and maintaining an on-site inventory of spare parts or other supplies necessary to make rapid repairs of the equipment.

The CEMS shall be in operation during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the device D1, except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments).

The CEMS shall be operated and maintained in accordance with the applicable quality assurance procedures required by 40 CFR Part 60 Appendix F and SCAQMD Rule 2011 Appendix A.

For every hour of invalid data, missing data must be substituted following the procedures in District Rule 2011, Appendix A, Chapter 2, Section E – Missing Data Procedures.

[**RULE 1303(b)(2)-Offset, 5-10-1996;** RULE 1303(b)(2)-Offset, 12-6-2002; **CONSENT DECREE CIVIL NO. 2:07CV134WL, 7-23-2007**]

[Devices subject to this condition: ~~**S17**~~ ***S151***]

E57.3 The operator shall vent this equipment to the sulfuric acid plant no. 4 whenever this equipment is in operation.

*[**RULE 1303(a)(1)-BACT, 5-10-1996;** RULE 1303(a)(1)-BACT, 12-6-2002]*

[Devices subject to this condition: C149]

H23.2 This equipment is subject to the applicable requirements of the following rules or regulations:

Contaminant	Rule	Rule/Subpart
PM	District Rule	1155

[RULE 1155, 12-4-2009]

[Devices subject to this condition: C54, C146, ***C148***]

BACKGROUND/HISTORY

Rhodia Inc., Carson facility (Rhodia) regenerates sulfuric acid for the refinery alkylation process and manufactures alum to be used as a flocculating agent in the drinking water purification and wastewater treatment plants. Rhodia currently operates one sulfuric acid plant, one alum (aluminum sulfate) manufacturing system and other equipment that associated with storage and handling of spent sulfuric acid and other raw materials.

Rhodia facility type:

RECLAIM SOx	RECLAIM NOx	Title V
Yes	Yes	Yes

Rhodia is a Title V facility. The renewal Title V Permit for the facility was issued on December 14, 2010.

On November 5, 2010, the Governing Board of the District adopted amendments to the RECLAIM program that would result in cumulative reductions of 5.7 tons per day, or more than 51 percent reduction, of oxides of sulfur (SOx) from all RECLAIM facilities by 2019. The changes are to be implemented in phases: 3 tons per day in 2013, 4 tons per day in each year from 2014 through 2016, 5 tons per day in 2017 and 2018, and 5.7 tons per day in 2019 and beyond.

Pursuant to the amended Rule 2002 (f)(1), the SOx RTC Holdings as of November 5, 2010 for Compliance Year 2013 and thereafter are adjusted by multiplying the amounts of the current RTC holdings by the following adjustment factors for the corresponding compliance years, to obtain tradable/usable and non-tradable/non-usable holdings:

Compliance Year	**Tradable/Usable RTC Adjustment Factor**	**Non-Tradable/Non-Usable RTC Adjustment Factor**
2013	0.7312	Not Applicable
2014	0.6416	Not Applicable
2015	0.6416	Not Applicable
2016	0.6416	Not Applicable
2017	0.5520	0.0896
2018	0.5520	0.0896
2019	0.4893	0.1523
All Years after 2019	0.4893	Not Applicable

Rhodia is one of a total of 15 SOx RTC holders, which are subject to adjustments of all their SOx RTC holdings. Based on the scheduled reduction, Rhodia's SOx RTC holdings will be trimmed from current 392 tons/yr to 191.8 tons/yr by 2019 (51% reduction).

In an effort to ensure early reductions in accordance with the RECLAIM Program, Rhodia proposed to install a wet scrubber. Thus, on October 20, 2010, Rhodia submitted two applications indicated as follows:

Appl. No.	**Type**	**Previous P/O**	**Equipment**	**Fee Sch.**	**Expedited?**
515638	P/C	N/A	Caustic Scrubber System	Sch. D	Yes
515640	Plan	N/A	N/A	RECLAIM/Title V Rev.	N/A

Appl. No. 515638 – Caustic Scrubber System

Application no. 515638 is submitted as an expedited permit application to install a caustic scrubber system to reduce the SOx emissions from the sulfuric acid plant. There will be no emission increase associated with this application.

Appl. No. 515640

Application no. 515640 is submitted as a plan for the minor revision of the Title V/Reclaim permit as specified in Rule 301.

PROCESS DESCRIPTION

Rhodia currently operates one sulfuric acid plant and one alum (aluminum sulfate) manufacturing system. The PM10 emissions (acid vapor) from the reactor of the alum manufacturing system are being controlled by a caustic scrubber. The PM 10 emissions from alumina trihydrate powder pneumatic conveying operation are being controlled by a bin vent filter. The PM10 (acid vapor) and VOC emissions associated with storage and handling of spent sulfuric acid are being controlled mainly by the furnace of the sulfuric acid plant. When the furnace is down, they are being controlled by a back-up air pollution control system consisting of caustic scrubbers followed by a flare.

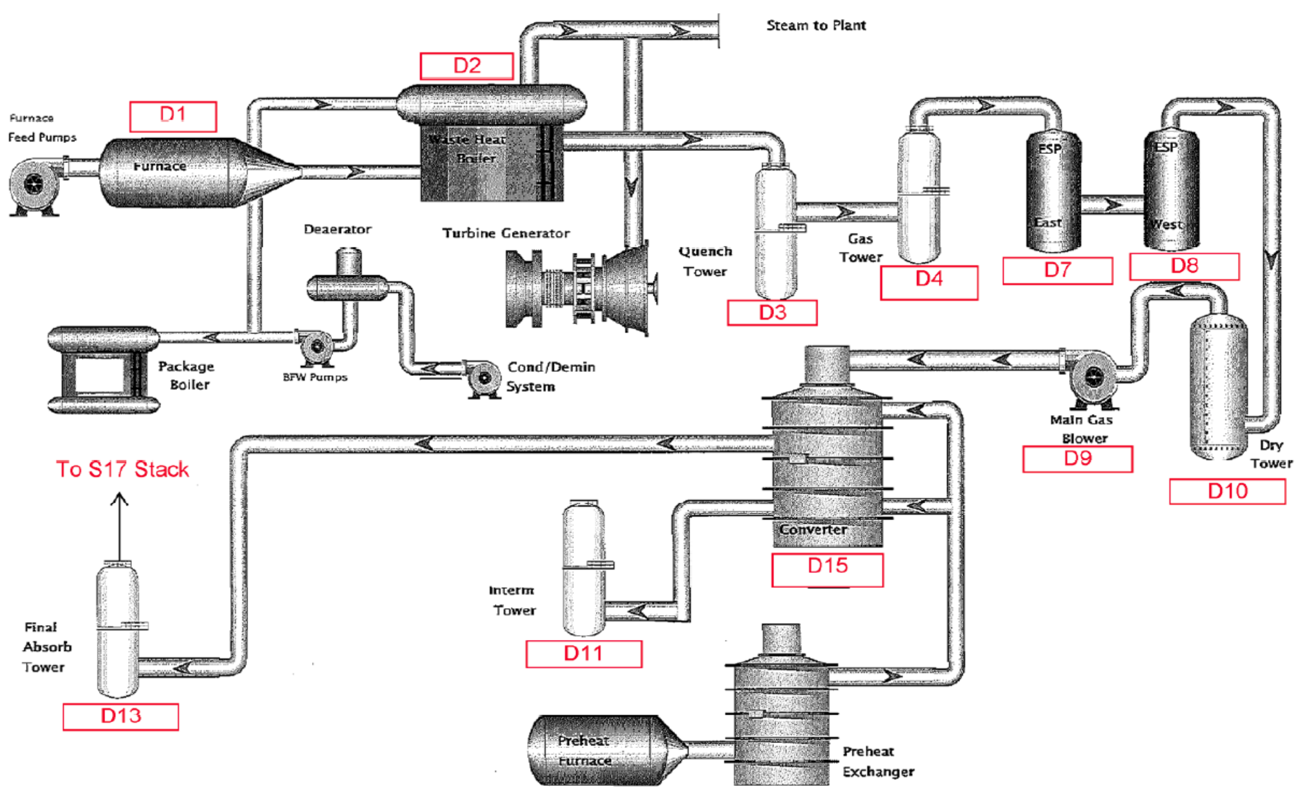

Fig 1
Rhodia Inc. Dominguez Plant
Process Flow Diagram

Spent sulfuric acid from refinery alkylation process and molten sulfur are injected into a natural gas fired furnace (D1). The spent acid is decomposed and sulfur is combusted to form a sulfur dioxide rich gas. The combustion gas products, including approximately 10 percent SO_2, pass through a waste heat boiler (D2) that generates steam to drive the main gas blower and other steam turbines in the plant. Dust and other impurities are removed by weak acid in a quench tower (D3), and the gas is cooled and partially dehumidified in a direct gas contact cooler (D4).

Two electrostatic precipitators (D7 and D8) remove sulfuric acid mist and the gas stream is completely dehumidified in a drying tower (D10). A steam turbine driven main gas blower (D9) forces the gas through the four stage catalytic converter/heat exchanger system (D15) where the vanadium based catalyst oxidizes the sulfur dioxide (SO2) to form sulfur trioxide (SO3). After the process gas passes through the first three stages of the catalytic converter, the sulfur trioxide is allowed to react with water to produce sulfuric acid in the intermediate absorption tower (D11). The gas makes a fourth pass through the catalytic converter to oxidize residual SO2, and is reacted in the final absorption tower (D13). The remaining gas, which consists of nitrogen, oxygen, carbon dioxide, a small amount of un-reacted SO2, and a small amount of nitrogen oxides, will be vented to the new scrubber system.

DOUBLE ABSORPTION TECHNOLOGY

The sulfur dioxide (SO_2) rich gas stream is catalytically oxidized to sulfur trioxide (SO_3) in a four stage converter/heat exchanger system. After the process gas passes through the first three stages of the catalytic converter, the SO_3 is allowed to react with water producing a 99% sulfuric acid solution in the intermediate absorption tower. With the SO_3 removed, a majority of the residual SO_2 is catalytically oxidized to SO_3 through the fourth pass. The SO_3 gas is absorbed in the final absorption tower, and the unconverted SO_2 is discharged into the atmosphere.

CAUSTIC SCRUBBER SYSTEM

The sulfuric acid plant tail gas, containing approximately 200 ppmV of SO_2, will be vent through a new wet scrubber system. The proposed wet gas scrubber system consists of a 2-stage wet gas caustic scrubber (C148), an acidulation tower (C149) and a caustic solution storage tank (C150). The wet scrubber uses a caustic or soda ash solution to remove the SO_2 from the tail gas as sodium salts (sodium sulfite/bisulfate). The acidulator is an effluent treatment unit, which will use sulfuric acid to convert the sodium sulfite/bisulfite in the scrubber salt solution to sodium sulfate. The sodium sulfate solution is then air stripped of dissolved SO_2. The SO_2 will be returned to the acid plant for processing. The acidulator is proposed because sodium sulfite/bisulfite are strong reducing agents with high effluent Chemical Oxygen Demand (COD) and not suitable for discharge; thus, they must be converted to sodium sulfate, which can be safely discharged to the onsite wastewater treatment system for disposal.

The tail gas leaves the sulfuric acid plant absorption tower high efficiency mist eliminator at about 150 - 180 ^{o}F and enters the bottom of a two stage scrubbing tower where the sulfur dioxide is absorbed and converted to a sodium sulfite/bisulfite/sulfate solution. The temperature is reduced to about 75 - 85 ^{o}F by saturation of the gas with water contained in the scrubbing solution.

The scrubber (C148) consists of two packed beds of packing, each independently irrigated with a sodium sulfite/bisulfite solution. A scrubber circulating pump is provided for each circulating loop with one additional pump as a common installed spare. Caustic (50%) solution required by the scrubbing system is pumped from the caustic storage/day tank to the upper stage solution circulating loop and intimately mixed in the circulating pump. Caustic is added to the top stage at a rate sufficient to reduce the SO_2 emissions to the required level.

Water is added to the top stage circulating system as make up for the water evaporation losses from the solution, and to maintain a constant salt content in the bottom stage solution, resulting in a specific gravity of less than 1.4. Excess solution from the upper stage overflows to the top of the lower packed bed. The gas leaving the upper packed scrubbing stage passes through an entrainment separator before entering the exhaust stack. The gas is saturated with water vapor and may under certain atmospheric conditions have a wet steam plume which will dissipate in a short distance.

Chemistry

Different forms of sodium salts are formed when SO_2 contact with sodium solution. Caustic (sodium hydroxide) reacts with the sulfur dioxide in the tail gas by the following reactions:

$$NaOH + SO_2 \rightarrow NaHSO_3$$
$$2\ NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2\ NaHSO_3$$
$$2\ NaOH + SO_2 + 1/2\ O_2 \rightarrow Na_2SO_4 + H_2O$$

Alternatively, soda ash (sodium carbonate) may be used to react with the sulfur dioxide in the tail gas by the following reactions:

$$Na_2CO_3 + 2\ SO_2 + H_2O \rightarrow 2\ NaHSO_3 + CO_2$$
$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$
$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2\ NaHSO_3$$

The system will be normally operated at a balance point to provide maximum sulfur dioxide removal with minimum caustic consumption. The lower stage is designed to operate with a high (approximately 6.5:1) bisulfite to sulfite ratio and a 10%-15% dissolved solids concentration to minimize caustic consumption and maintain bisulfite solution far away from saturation, while the upper stage is operated with a low bisulfate to sulfite ratio and a low dissolved solids concentration to maximize sulfur dioxide removal.

Caustic scrubber packing components:

Tower cross-section	177	ft^2
Liquid	600-1200	GPM
Air flow	10,000 – 70,000	SCFM
Packing height	>12	ft
Packing material	STD/LPD Saddles, or Hy-Flow/Pall Rings	
CFM/ft^2	56 - 395	
GPM/ft^2	3.40 – 6.80	
ΔP	1 -3	in H_2O/ft

Acidulation Stripping

In the acidulation stripping system (C150), the sodium sulfite/bisulfite solution from the scrubber is treated with sulfuric acid to produce a sodium sulfate solution with dissolved sulfur dioxide. The dissolved sulfur dioxide is removed from the solution by air stripping, and is recycled to the sulfuric acid plant for processing. The stripping airstream will be created by suction of the main gas compressor (D9). The moisture contents in the stripping airstream will be removed by the drying absorber (D10).

The chemical reactions that occur in the acidulation process are:

$$2\ NaHSO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ SO_2 + 2\ H_2O$$
$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + H_2O$$

The above acidulation reactions occur in the in-line mixer and also at the upper section of the stripper. Sulfur dioxide is air stripped from the acidic sodium sulfate solution in the packed section of the tower. The stripper bottoms pump provides a recycle liquid stream to the stripper inlet to maintain minimum liquid flow to the stripper packing at high plant turndown. The stripper bottoms are discharged on level control to the existing plant effluent treatment system.

Air is drawn into the stripper by the negative pressure (created by suction force of the main air compressor D9) at the inlet to the drying tower (D10), and is used to strip SO_2 from the sodium sulfate solution. The combined gas stream, containing air and sulfur dioxide, is returned to the sulfuric acid plant at the inlet to the drying tower for reprocessing.

Caustic Storage/Day Tank

A new 7,000-gallon carbon steel storage tank (C150) will be installed to provide caustic supply for the proposed wet scrubber. Caustic (10-50%) is received-transferred from the existing plant’s 95,000-gallon caustic storage tank to the new caustic storage facility. The caustic is fed to the SO_2 scrubbing tower by a positive displacement diaphragm pump with spare at the rate required by the SO_2 scrubber. The caustic tank and lines are insulated and electrically heated and traced to maintain the caustic solution at a temperature greater than 90 F to reduce viscosity and prevent freezing.

EMISSION CALCULATIONS

This application is to install a caustic scrubber system to reduce SO_2 emissions from the sulfuric acid plant. There will be no emission increase associated with this application.

However, system condition nos. S42.1, D82.2 and D82.3 specifies an equation for the operator to calculate SO_2 emissions; thus, it is necessary to re-exam its applicability.

Condition No. S42.1 limits the sulfuric acid plant SO_2 emissions at 3.5 lbs per ton of 100% H_2SO_4 produced and the compliance shall be determined using the following equations:

$$E = \frac{1306}{X_e} - 1306 \quad \text{.. Equation 1}$$

Where: E = SO_2 emission rate in lbs per ton of 100% H_2SO_4 produced

$X_e = fractional\ conversion\ efficiency = \frac{M_1 - M_2}{M_1 - 1.5 M_1 M_2}$ .... Equation 1a

Where: M_1 = the fractional concentration of SO_2 entering the converter
M_2 = the fractional concentration of SO_2 at the stack

Condition nos. D82.2 and D82.3 require the operator to install and maintain CEMS to monitor SO_2 concentrations at inlet of the converters (compressor D9) and outlet of the acid absorber (stack S17).

Equations 1 and 1a are derived based on the following chemical reaction:

$SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4$ .... Reaction 1

Equation 1

Molecular weight of SO_2 = 64.07 lbs/lb-mole
Molecular weight of H_2SO_4 = 98.086 lbs/lb-mole

$$\frac{2{,}000 \text{ lbs } H_2SO_4}{1 \text{ ton } H_2SO_4} \left| \frac{1 \text{ lb-mole } H_2SO_4}{98.086 \text{ lbs } H_2SO_4} \right| \frac{1 \text{ lb-mole } SO_2}{1 \text{ lb-mole } H_2SO_4} \left| \frac{64.07 \text{ lbs } SO_2}{1 \text{ lb-mole } SO_2} \right. = 1{,}306 \text{ lbs } SO_2 \text{ are required per ton } H_2SO_4$$

$$E = \frac{(\text{Unconverted } SO_2\text{, lbs})}{1 \text{ ton } 100\% \ H_2SO_4}$$

$$= \frac{\frac{(\text{Converted } SO_2\text{, lbs})}{X_e} - (\text{Converted } SO_2\text{, lbs})}{1 \text{ ton } 100\% \ H_2SO_4}$$

$$= \frac{1{,}306 \text{ lbs converted } SO_2 \text{ per ton } 100\% \ H_2SO_4}{X_e} - 1{,}306 \text{ lbs converted } SO_2 \text{ per ton } 100\% \ H_2SO_4$$

Equation 1a

$$M_1 = \frac{\text{Converter Inlet } SO_2\text{, Moles/hr}}{\text{Total Converter Inlet Air, Moles/hr}}$$

$$M_2 = \frac{\text{Unconverted } SO_2 \text{ at stack, Moles/hr}}{(\text{Total Converter Inlet Air, Moles/hr}) - (\text{Converted } SO_2\text{, Moles/hr}) - (O_2 \text{ participated in the reaction, Moles/hr})}$$

$$= \frac{(\text{Converter Inlet } SO_2\text{, Moles/hr})\ (1 - X_e)}{(\text{Total Converter Inlet Air, Moles/hr}) - (1.5)\ (\text{Converter Inlet } SO_2\text{, Moles/hr})\ (X_e)}$$

Re-arrange the two equations above, equation 1a is obtained.

Based on the analysis presented above, this writer concluded the following conditions have to be true for equation nos. 1 and 1a:

1. The reduced amount of SO_2 from inlet air stream are all converted to H_2SO_4
2. The inlet and outlet SO_2 concentrations (M1 and M2) shall be measured on a dry basis
3. Only SO_3 and no other gas will be generated between the inlet monitoring location (M1) and outlet monitoring location (M2)

The installation of the caustic scrubber system and the relocation M2 monitoring device from stack S17 to the scrubber stack S151 will affect these conditions; the changes to these conditions are summarized as follows:

1. Additional SO_2 removal caused by the new caustic scrubber (C149) is actually not converted to H_2SO_4. However, since the converter and absorbers will reduce SO_2 concentrations from 10% to 200 ppmv, and from 200 ppmv the caustic scrubber will further reduce to 100 ppm or lower by 2019; thus, this additional removal as compared to total removal efficiency (X_e) is insignificant (one in a thousand).
2. The new stack S151 exhaust air stream will be moisture laden. However, since the CMES SO_2 analyzer is measuring concentration on dry basis, no effect on these equations. Conditions D82.2 and D82.3 will be changed to reflect the dry basis measuring.
3. Additional acid-base reactions will occur in the scrubber. If soda ash ($NaCO_3$) is used to produce caustic solution, CO_2 will be generated during the scrubber acid-base reactions. Additional CO_2 will dilute the concentration measurement of M2. However, due to the caustic scrubber will only reduce SO_2 concentration from 200 ppm to 100 ppm or lower by 2019, and one mole SO_2 will produce a maximum of one mole CO_2, the degree of dilution of M2 is insignificant.

In addition, the measurement of M1 will not be affected by the additional SO_2 generated by the stripper (C150) because M1 is measured at the gas compressor (D9) inlet, which is after the stripper generated SO_2 merges with the mainstream SO_2 at the drying absorber (D10).

CAUSTIC SCRUBBER SYSTEM

The basic chemistry for the caustic scrubber is indicated as following:

$$NaOH + SO_2 \rightarrow NaHSO_3$$
$$2\ NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2\ NaHSO_3$$
$$2\ NaOH + SO_2 + 1/2\ O_2 \rightarrow Na_2SO_4 + H_2O$$

Caustic scrubber:

Tower cross-section	177	ft^2
Liquid	600-1200	GPM
Air flow	10,000 – 70,000	SCFM
Packing height	>12	ft
Packing material	STD/LPD Saddles, or Hy-Flow/Pall Rings	
CFM/ft^2	56 - 395	

GPM/ft^2	3.40 – 6.80	
ΔP	1 -3	in H_2O/ft

Scrubber Efficiency Calculation

Assume the interface gas film concentration (y_i) is zero, the height of column is calculated by:

$$Z = H_g \int_{y_2}^{y_1} \frac{dy}{y}$$

where Z = height of packing column in ft
H_g = HTU for gas resistance in ft
y_1 = each scrubber inlet molar gas concentration
y_2 = each scrubber outlet molar gas concentration

$H_g \approx H_{og}$ = 2.5 ft (Form 400-E-3)
Z = 12 ft

$\ln \frac{y_1}{y_2}$ = (12 ft) / (2.5 ft) = 4.8, and $\frac{y_1}{y_2} = 121.51$

Theoretical control efficiency for the scrubber = 1 – 1/(121.51) = 99.18%

The above control efficiency is calculated based on an assumption of the acid-base reaction plane coincides with the gas-liquid interface, and the absorption becomes completely limited by the gas film. However, this assumption may be too optimistic for this scrubber because much of the film spaces are occupied by HSO_3^-, which slows down the liquid phase reaction or diffusion kinetics. This is especially true for the lower stage scrubber, where Rhodia wants minimize the cost by minimizing caustic consumption and maintain maximum HSO_3^- contents.

The majority upper stage scrubber chemical reactions are indicated as follows:

$$NaOH + SO_2 \rightarrow NaHSO_3$$
$$2\ NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

The majority lower stage scrubber chemical reactions are indicated as follows:

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2\ NaHSO_3$$

Rhodia provided the following equations for the equilibrium partial pressure of sulfur dioxide over sodium sulfite/bisulfite solutions. The equilibrium data is based on the work of Professor H.F. Johnstone of the University of Illinois.

$$P_{SO_2} = \frac{M(2S-C)^2}{C-S} \quad \text{.......... Equation 2}$$

Where:
Log M = 4.519 – 1987/T, and pH = 9.2 - 4.62 S/C
P_{SO2} = Equilibrium partial pressure of SO_2, mmHg
S = Moles of S / 100 moles H_2O
C = Moles of Na / 100 moles H_2O
T = degrees K

Note: S/C of 0.5 is 100% sulfite, and S/C of 1.0 is 100% bisulfite. The operating solution in the scrubber is a mixture of sulfite and bisulfite in water solution.

The references to Johnstone publications are:

- Johnstone, H.F., etal, Recovery of Sulfur Dioxide from Waste Gas, Industrial and Engineering Chemistry, Vol 27, No 5, May 1935, pp 587-593.
- Johnstone, H.F., etal, Recovery of Sulfur Dioxide from Waste Gas, Industrial and Engineering Chemistry, Vol 30, No 1, January 1938, pp 101-109.

Equation no. 2 shows that a careful balance between the injection speed of sodium contents and the removal speed of sulfur contents will allow Rhodia to operate the sulfuric acid plant at any desirable SO_2 emission level, which is most likely to be at a level of lowest cost to the company. In any event, SO_2 emissions will not increase with the addition of the caustic scrubber and the emission levels will be monitored under a continuous emission monitoring system (CEMS). It is not necessary to impose any parameter control conditions.

RULES AND REGULATIONS EVALUATION

CEQA: **California Environmental Quality Act** – CEQA requires that the environmental impacts of proposed projects be evaluated and that feasible methods to reduce, avoid or eliminate identified significant adverse impacts of these projects be considered. The CEQA Applicability Form (400-CEQA) indicates that the project has impacts which trigger the preparation of CEQA document.

A CEQA document was prepared and the District is currently in the reviewing process.

Rule 212: **Standards for Approving Permits** – The facility is not located within 1,000 feet of a K-12 school. In addition, the caustic scrubber system will be installed to reduce SOx emissions; thus, no emission increases are expected. A Public Notice is not required.

Rule 401: **Visible Emissions** – Compliance is expected from well maintained and properly operated equipment.

Rule 402: **Public Nuisance** – The potential for public nuisance from the operation of this equipment is minimal. The facility is located in an industrial area.

Rule 469: **Sulfuric Acid Unit**

The SOx emission requirements of this rule are exempt for the subject sulfuric acid plant per Rule 2001 (j) – Table 2.

Rule 1155: **Particulate Matter (PM) Control Devices**

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Section (d)(1) requires all PM air pollution control devices not to have any visible emissions. Compliance is expected from well maintained and properly operated equipment. In addition, condition no. H23.2 is added to ensure compliance of this requirement.

Section (d)(3) requires this equipment to be operated and maintained in accordance with the manufacturer's operation and maintenance manual or other similar written materials. Compliance is expected.

Sections (e) and (f) - Monitoring and Record Keeping Requirements. Compliance with this rule is expected. Condition no. H23.2 is added to ensure compliance of these requirements.

REG XIII: Rhodia is operating under the RECLAIM program, the NOx and SOx emissions are not subject to Regulation XIII per Rule 1301(b)(1).

BACT – the caustic scrubber system will be installed to reduce SOx emissions from the sulfuric acid plant; thus, no emission increases for other pollutants are expected. BACT is not required.

Offset – Offsets are not required for this facility since the criteria contaminant emissions will not exceed the limits in table A (rule 1304(d))

	VOC (lb/day)	PM10 (lb/day)	NOX (lb/day)	CO (lb/day)	SOX (lb/day)
Current NSR (PTE)	**2**	**0**	**N/A**	**3**	**N/A**
515639 – Caustic Scrubber System	**+0**	**+0**	**N/A**	**+0**	**N/A**
Total PTE	**2**	**0**	**N/A**	**3**	**N/A**
Threshold limit	**22**	**22**	**N/A**	**159**	**N/A**
Offset required	**N/A**	**0**	**N/A**	**0**	**N/A**

RULE 2002: **Allocations for Oxides of Nitrogen (NOx) and Oxides of Sulfur (SOx)**

(f)(1)(I) – the annual allocations for SOx for Rhodia will be trimmed from current 392 tons/yr to 191.8 tons/yr by 2019 (51% reduction). After the installation of the proposed caustic scrubber system, Rhodia will be able to meet its annual allocation requirement.

RULE 2005: **New Source Review for RECLAIM**

There is no emission increase associated with the proposed caustic scrubber system. BACT is not required.

RULE 2011: **Requirements for Monitoring, Reporting, and Recordkeeping for Oxides of Sulfur (SOx) Emissions**

There is no emission increase associated with the proposed caustic scrubber system. No emission offset is required.

RULE 2012: Requirements for Monitoring, Reporting, and Recordkeeping for Oxides of Nitrogen (NOx) Emissions

There is no emission increase associated with the proposed caustic scrubber system. No emission offset is required.

Reg XXX: Title V Permit

Rhodia Inc.facility (Facility ID: 114801) has an active Title V permit. Based on the above evaluation, the proposed scrubber will not cause any emission increases. Therefore, application no. 515640 is considered “minor permit revision” of Title V Facility Permit and it is subject to a 45-day EPA review prior to final revision of the Title V Facility Permit (Application No. 515640).

CONCLUSION AND RECOMMENDATIONS

Based on my evaluation, the subject equipment will operate in compliance with all applicable District Rules and Regulations. A Permit to Construct is recommended.